

All-hydrocarbon Composite Resins Based on Cyclopentadiene

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Introduction

Currently available resins for normal and demanding composite applications often suffer from swelling and/or degradation caused by polar organic solvents and hot, wet environments. One possible means of overcoming these disadvantages is to use all-hydrocarbon matrices that inherently limit interaction and penetration by both organic solvents and water. Polybutadiene is an example of a resin whose inherent hydrophobicity provides excellent hot-wet stability and long term resistance to moisture and saline environments; its use in composites has been limited, however, because of poor physical properties at ambient temperature.¹ We have developed an alternative, inexpensive resin based on multiply-substituted cyclopentadienes. Multiple substitutions of electrophiles onto cyclopentadiene anions have been shown to be quite facile and generate high degrees of substitution.^{2,3,4} It has been found that reactions of cyclopentadiene anions with electrophiles possessing terminal unsaturation generate resins which possess low viscosities, ready thermal cure under catalyzed and non-catalyzed conditions, and excellent mechanical, physical and chemical properties in composites with glass and carbon fibers.

Experimental

The resin synthesis is straight-forward and versatile. Dicyclopentadiene was thermally cracked to cyclopentadiene which was then reacted neat with alkenyl or alkynyl halides and base in the presence of a phase transfer catalyst. The general synthetic route for the formation of the cyclopentadiene based resins is outlined in Figure 1. Electrophiles such as allyl chloride, propargyl chloride and undecylenyl bromide were reacted neat with the cyclopentadiene anion generated from concentrated aqueous KOH and tetrabutylammonium bromide under rapid stirring and cooling as needed. The electrophiles were reacted individually and as mixtures in the feed. Products of the reaction were extracted with methylene chloride and the phase transfer catalyst removed by washing with methanol/water. Column chromatography was sometimes used to obtain very pure material and yields of the reactions were quantitative. A mixture of isomers of multiply substituted cyclopentadienes was obtained with degrees of substitution ranging from 2-6 depending on the electrophile(s) used. Gas chromatography was used to monitor the reactions and to analyze product composition. Mixtures of electrophiles gave mixtures of multiply-substituted derivatives with various combinations of the two pendent groups; eg., both

3:1 and 7:1 mixtures of allyl to propargyl chlorides gave high yields of mixed products (APCPs).

Results and Discussion

Figure 2 gives the DSC traces of various resin systems. Surprisingly, pure ACP cures without added initiator, showing a maximum exotherm at ca 250°C. When the sulfonium salt, 1-(p-decyloxybenzyl)tetrahydrothiophenium hexafluoroantimonate (DTHA), was used, much faster cationic cure took place with an exotherm at approximately 110°C. The 3:1 APCP resin underwent a non-catalyzed partial cure at 115 °C followed by complete cure at 200-300 °C. The first exotherm is consistent with the spontaneous cure of pure PCP resin.

FTIR was used to monitor the cure reaction of a neat 7:1 APCP resin. Figure 3 gives traces after heating the same sample for 1 hour at the temperatures indicated using a variable temperature IR cell. The characteristic peaks for alkyne and alkene CH units were seen at ca 3300 and 3075 cm⁻¹. Gradual disappearance of these peaks with thermal reaction is consistent with polyaddition reactions involving free radical polymerization, ene-like rearrangement-addition reactions and/or Diels-Alder cycloadditions. The exact mechanism or combination of mechanisms involved with the cure of these resins is currently under study. It is clear, however, that there is an overall decrease in the amount of unsaturation present in the cured materials, a result confirmed by solid state ¹³C NMR analysis. This implies formation of final structures that should possess low dielectric constants, a highly crosslinked nature and very low affinity for water and polar penetrants.

Mechanical analyses of composites formed from these resins showed excellent properties. For example, Figure 4 gives the three point flexure results for pure ACP with carbon and glass fibers along with a glass composite made with amine-cured epoxy. The flexure moduli of the ACP materials were significantly higher than the epoxy composite, although failure was more catastrophic to give lower overall toughness. This behavior is again consistent with formation of a highly crosslinked and brittle network. Work underway (but not discussed here) has shown that use of UCP and AUCP resins successfully improves flexibility and toughness but with a reduction in modulus. Dynamic mechanical and thermogravimetric analyses of composites made with these new resins indicates loss of roughly only half the initial modulus at 300 °C (going from 65 to 42 GPa) with the former and no weight loss below 400 °C. For comparison, the analogous epoxy composite lost virtually all mechanical properties by 200 °C.⁵

In conclusion, we have developed a general synthesis of reactive all-hydrocarbon composite resins containing a variety of unsaturated substituents that allow tailoring of the rate of cure through cationically-initiated or non-initiated thermal polyaddition and crosslinking reactions. Glass and carbon fiber composites made with these resins show better room temperature moduli and much better high temperature properties (modulus and thermal stability) than epoxy-based analogs. Intense effort

is underway to further evaluate the resin synthesis, cure conditions and composite properties.

Acknowledgements

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References

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5. The epoxy composite was 70 wt-% glass fibers with Shell Epon 828 cured with methylene dianiline at 55 °C/16 h, 175 °C/2 h and 200 °C/4 h.

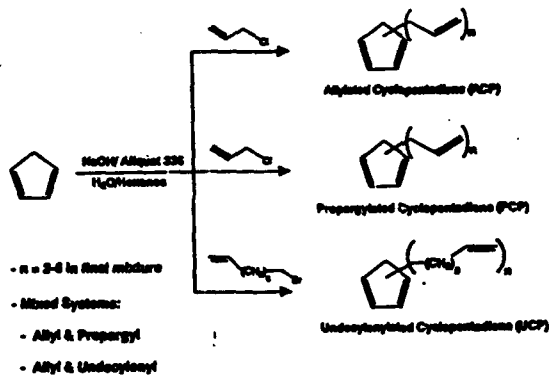


Figure 1. Reaction Schemes

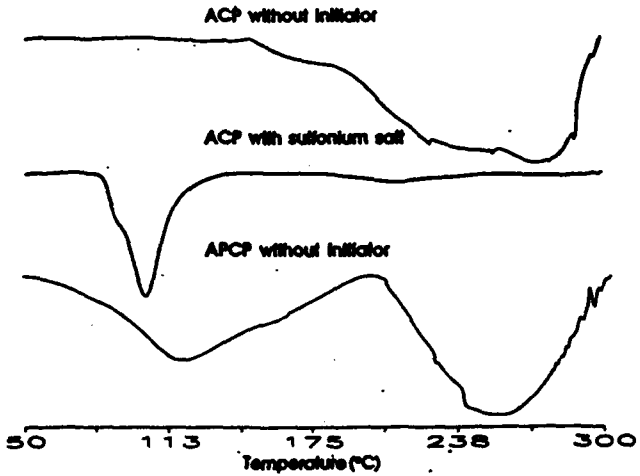


Figure 2. DSC Traces of ACP and APCP Heated at 10 °C/min

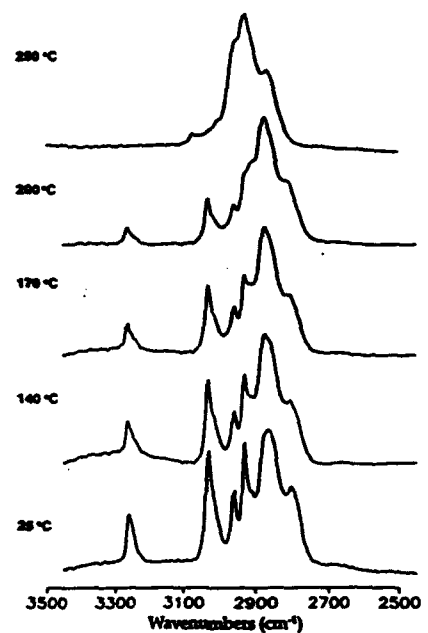


Figure 3. FT-IR Spectra of Neat 7:1 ACP Resin Heated 1 Hour at Indicated Temperatures

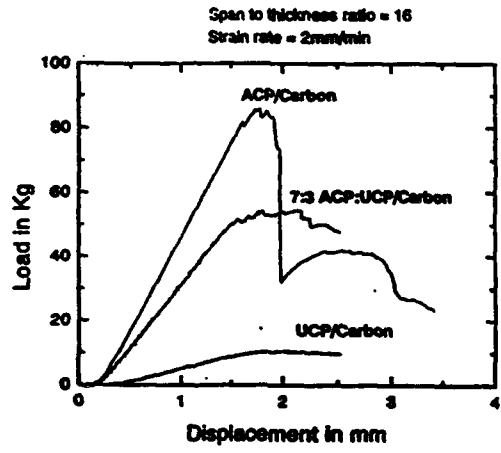


Figure 4. MTS Three Point Flexure Results

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